Energy-level alignment of Ru complex on SAM films probed by frequency-modulation EFM combined with Fowler-Nordheim tunneling spectroscopy

M. Nakayama,[1#] T. Misaka,[1] H. Ohoyama,[1] and T. Matsumoto[1]

[1]*Departmen of Chemistry, University of Osaka, Toyonaka, 560-0043, Japan*

Presenting author's e-mail: nakayamam21@chem.sci.osaka-u.ac.jp

Organic electronics utilize molecular components for charge transport, leveraging their diverse functionalities to achieve enhanced performance. Key examples include OFETs and OLEDs, where understanding charge transfer from electrodes is crucial for their operation. Self-assembled monolayers (SAMs), consisting of single molecules, are often used to control the conductivity of devices. However, properties such as the work function, electrostatic potential, and energy level alignment on SAMs remain unclear. In this study, we used electrostatic force microscopy (EFM) to investigate the average electrostatic potential and molecular energy levels in SAM-based organic multilayer films. SAMs were formed by immersing Au(111)/mica substrates in ethanol solutions of either 6-amino-1-hexanethiol (6-AHT) or 11-amino-1-undecanethiol(11-AUT), followed by adsorption of a Ru complex (N719). EFM measurements revealed the release of electrostatic energy through the tunneling processes at a sample bias voltage (V_b) higher than $|V_b| = 5$ V for 6-AHT and N719/6-AHT/Au samples, whereas 11-AUT-based samples showed no release of electrostatic energy. The observed electrostatic potential at the V_b region with no tunneling effect agreed with the predictions using a single-capacitor model incorporating SAM coverage data from XPS. In the N719/6-AHT/Au system, V_b dependence of the released electrostatic energy at the negative V_b region can be well reproduced by Simmons' tunneling model. In contrast, the positive V_b region follows a resonant tunneling model, suggesting electron transport via the LUMO of N719. This analysis also gives information on a partitioning factor β of V_b between N719 and SAM [1]. These findings deepen the molecular-level understanding of the charge transport processes in organic electronic devices.

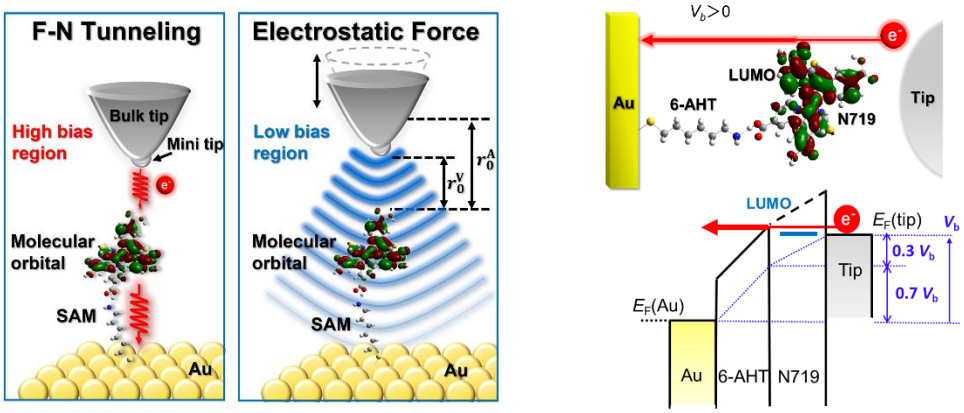

Figure 1. Schematic of the combination of EFM and Fowler-Nordheim tunneling spectroscopy(left) and Schematic energy diagram for N719/6-AHT/Au (right)

Reference

[1] M. Nakayama, et al. ACS Appl. Mater. Interfaces. **15**, 47704 (2023).